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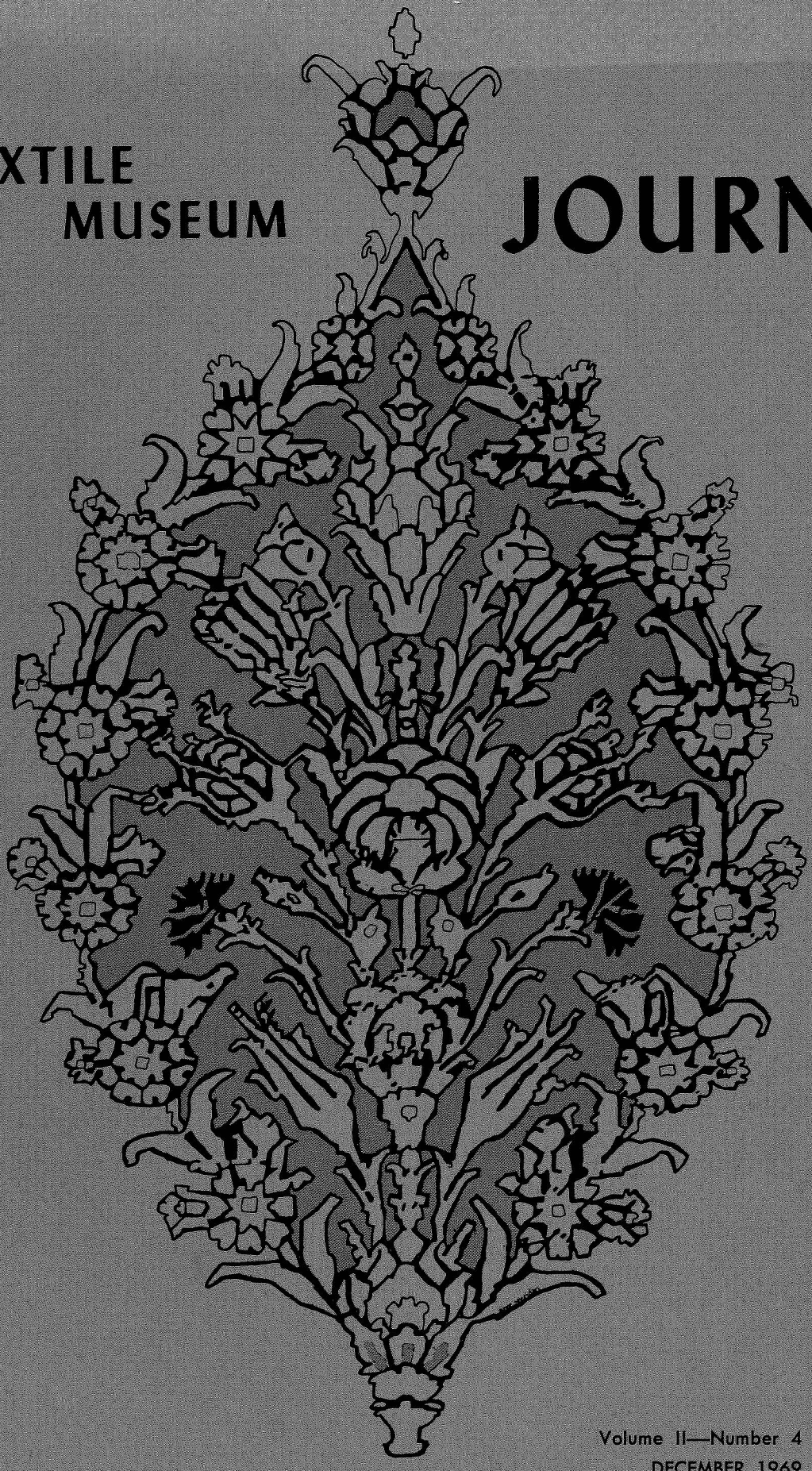

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COVER: Drawing by Anne Sheridan of the large floral oval wreath designed in the center of Textile Museum's "Benguiat" Ottoman prayer rug, 1967.24.1 (Figure 13 in Charles Grant Ellis' article "The Ottoman Prayer Rugs").

DRAWINGS for Color-relationship Chart and illustrations for "How to Match Colors when Dyeing Yarns or Fabrics for Textile Conservation Purposes" by Col. James W. Rice are by Dianne Sisko.
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PRINCIPLES OF TEXTILE CONSERVATION SCIENCE NO. XI

REQUIREMENTS FOR BULK STORAGE PROTECTION AGAINST INSECT DAMAGE

JAMES W. RICE

Requirements for sealed bulk storage protection against fabric damaging insects are generally limited to structural features such as air tight vaults, either metal lined or of finished masonry with tight door closures. These not only keep out the insects but also serve to protect the stored articles from theft, fire, and accidents. In addition, the construction and management of storage vaults provide means of maintaining equalized temperature and humidity conditions. A temperature of about 40° F. is expected to discourage moths and various beetles, although some species of the latter will withstand temperatures even as low as 18° F.

The relative humidity in such a vault must be lower than 70% to prevent mildew growths and is usually maintained at 50% or below as a margin of safety. This fungus control is most important for discouraging infestations of termites, book lice (psocids) and other cellulose damaging insects.

Since storage in the dark is the usual practice, the low temperatures and hu ities are beneficial in extending the textile or specimen life. However, there is always the possibility of introducing contaminating insects, spores, bacteria, or germs into such a sealed bulk storage when it is opened for removal of articles or inspection, and especially when new things are moved in. In this case, the vault must be considered as being contaminated and, at this point, a new question arises.

How Can a Sealed Storage Vault or Space be Decontaminated?

There are two practical methods of decontamination. The first, called the temperature shock treatment, is effective for control of moths and carpet beetles. To do this, the room temperature is lowered to 18° F. and then raised to 50° and again lowered to 18° F. This kills the moth and beetle eggs and larvae. The temperature of the room is then maintained at 40° F. This system is satisfactory and eminently suitable for fur and does not entail health hazards to personnel, and, once installed, maintenance is relatively inexpensive.

The second method is that of fumigation and is further explained by the following questions and answers.

What is Fumigation?

Fumigation is a name for getting rid of insect pests, spores, bacteria and germs by means of toxic or repellent gases or vapors. We must either drive the unwanted insects or organisms away, make them sick, or kill them. It is a pest control method that has been used with success where the operators are trained in the work and know the characteristics of the fumigant. It has also been abused and has failed because of ignorance and carelessness.

What are the Necessary Properties for an Acceptable Fumigant?

The principal characteristics for a fumigant are:

1. It should be lethal in a reasonable concentration to all of the various insects which one may expect to encounter in the geographic region where the specimen is kept. This means that it should kill eggs, larvae, adults and the various instar or moult forms. Therefore, a mere repellent may not necessarily be an efficient insecticide.

An ideal fumigant would be one that would not be toxic to human beings or warm-blooded animals, but since there are very few substances that will act on all insects and not on man in some way, we may not realize this ideal. So one must be chosen that can be tolerated.

2. It must be volatile, so that enough poison can be gotten into the air to affect the insect form. Some otherwise very powerful insecticides are non-volatile and thus can only do their job if the insect comes in actual physical contact with them. These are usually too persistent and may cause the fabric sample to be contaminated with substances harmful to human beings. Thus a vapor or gas must do its job and then escape without leaving a toxic residue.

3. In a similar way, the fumigant gas or vapor must have high penetrating powers. This means that in order to get to the interior of a padded structure such as upholstered furniture, the molecule must be quite active. Activity may be estimated as inversely proportional to the square root of the molecular weight (Graham's Law). This physio-chemical law which deals with permeability of membranes explains why some fumigants may be expected to kill the eggs within a reasonable time exposure whereas others, like pyrethrum, which are very effective in knockdown or killing of adult forms on contact, may not produce results on the eggs.

4. The fumigant must not damage or react adversely with the fabric materials or their coloring matter. Thus sulfur dioxide or fumes from burning sulfur candles, which is one of the oldest of the fumigants, is not recommended because it may destroy or otherwise affect some colors and it also has been accused of degrading cellulosic fibers. Similarly, some of the organic bromides which are reputed to have remarkable toxic effects on beetle larvae, adults and eggs, have been found to generate vile and persistent residual odors in rubber, and some leathers and wools. These may be the result of chemical reactions with sulfur containing vulcanizing or tanning agents or dyestuffs to form mercaptan-like substances which are noted for their disgusting odors. As for affecting colors, paradichlorobenzene ($C_6H_4Cl_2$), the ingredient used in aromatic moth crystals, has been found to fade or change the color of some cellulose acetate dyes during storage.

5. The fumigant should not be explosive or flammable. In this respect, carbon disulfide (CS_2), which is very effective for control of ants and rodents in burrows, for example, is considered too explosive to be used except in unusual and carefully controlled cases. On the other hand, ethylene oxide (C_2H_4O), which may be dangerously explosive when used alone, becomes relatively explosion-safe when mixed with inert gases like carbon dioxide or the Freons at about 89 to 90% of the inert by weight. (Freons are a group of fluorinated hydrocarbons much used as expellents in canned foams and instant sprays. Freon is a trademark name for such substances produced by the E. I. du Pont de Nemours Co.)

What are Some of the Advantages and Disadvantages of the Widely Known Fumigrants?

1. Hydrocyanic acid gas HCN is one of the most dangerous and rapid poisons known. Because of its low molecular weight (F.W. 27), it is slightly more penetrating than air (F.W. av. 29), but less so than water vapor (F.W. 18). Because of this property, it will pass through egg membrane structures rapidly, It has a distinctive odor resembling bitter almond which can be detected at very low concentrations; but, in order to kill, it must be present at a certain concentration level where it is higher than the odor threshold concentration. For this reason its presence may be detected by human beings before it kills. This is not an absolute safety warning because many experienced fumigation workers have been known to have lost their lives, probably because of overconfidence in this respect.

In the past, it has been used to fumigate ships, warehouses, and buildings which can be sealed up tight. The gas may be generated by action of acid on sodium or potassium cyanides which are crystalline salts or may be released from wafers which are saturated with a solution of the gas. Enough to produce a concentration of about 24 ounces per 1,000 cubic feet of space is used. The usual exposure time is 24 hours to allow for natural penetration through thick layers of materials and into nooks and crannies. At least 24 hours of airing with many successive changes of air is necessary before the space can be occupied. Personnel engaged in the work must be equipped with gas masks which have special HCN type cannisters. Even these do not furnish absolute protection, because the gas is so active that it may be absorbed through the skin.

Fumigation of large spaces with this gas is very dangerous and hard to control and for that reason is very costly. It is not recommended because of these factors. It is practical, however, for small chambers that can be quickly and positively sealed, locked, and ventilated readily afterwards. The dangers of clearing and time in this case may be minimized by venting the spent fumes high into the air by a forced draft fan and stack.

Ethylene oxide, C_2H_4O, is a modern space fumigant of low molecular weight (F.S. 44) which, according to Graham's Law estimates, may be expected to be less penetrating than air but superior to many other toxic gases and fumigants. It has the same molecular weight as carbon dioxide (CO_2) with which it may be diluted for practical use and to minimize its explosiveness. As a 90% CO_2—10% C_2H_4O mixture, it may be purchased compressed in cylinders under the trade name "Carboxide" [1] or it may be obtained in cans mixed with 89% of commercial expellant under the trade name "Cryoxcide".[2]

These mixtures have been used as both insecticides and fungicides for foodstuffs and have been found to be effective sterilizing agents for surgical appliances and apparel which will not withstand high temperatures or steam treatments.

They have been used for fumigation of overstuffed furniture, bedding, rugs, and other fabrics in controlling beetles, roaches, and bedbugs at the rate of 30 pounds of mixture for 12 hours' exposure or 10 pounds of mixture for 48 hours' exposure in sealed chambers or vaults. This usuage rate would have to be increased, however, where fumigation of a large building space or warehouse that cannot be tightly sealed is attempted. Egg destruction may be expected at the higher concentrations and longer exposures.

Ethylene oxide is much less toxic to human beings than many of the other fumigants. For example, it is rated roughly one-fifth as dangerous as methyl bromide, or four-fifths as hazardous as ethylene dichloride, both of which are widely used in commercial fumigating mixtures.[3] Needless to say, it is also very much less toxic than hydrocyanic acid gas. Other than its explosiveness, which can be overcome, and its cost, it is a very good fumigant because it leaves no bad after-effects in the specimen and overcomes many pest conditions which other insecticides may not affect.

Methyl bromide CH_3Br (F.W. 95), sometimes called bromomethane, is a widely used and effective insecticide and fumigant. It is quite poisonous and is rated [3] as being about five times as danger-

ous to human beings as chloroform which is about equal to ethylene oxide in general toxicity. Although it is rated as a very penetrating gas, it is roughly about one-sixth as rapid as air, if compared according to Graham's Law estimates. Because it is quite soluble in many substances, this comparison may not express its precise activity. At any rate, it is reputed to attack all stages of insect life, including the eggs, and, since its toxicity is high, the net efficiency as an insecticide is probably very good. For various reasons, it is often mixed with chlorinated hydrocarbon solvents, one of the more widely used of which is carbon tetrachloride $C Cl_4$ (F.W. 153.8).

Another additive that has been employed as a safety indicator is chlorpicrin ($C Cl_3NO_2$) which was used for a time in World War I as a tear gas. Its effect on the eyes is so unbearable in very low concentrations, that personnel can detect the presence of the fumigant long before it may be dangerous. The chlorpicrin itself is quite toxic towards certain plant pests and has been used alone in open air for insect control on sugar plantations. A mixture of 80% methyl bromide—20% chlorpicrin, called Picride [4] is said to be effective for space where tight seals are uncertain. The chlorpicrin is more persistent than methyl bromide and a longer time of aeration after fumigation is required when it is used.

Ethylene dibromide or dibromo ethane ($C_2H_4Br_2$) (F.W. 187.9) is another toxic bromine hydrocarbon used extensively in fumigation. Mixtures of 5 to 15% in carbon tetrachloride [5] have been used successfully for grain fumigation. It is probably less toxic than methyl bromide and less penetrating, but may react with rubbers, leathers, and skins of certain tanning processes, and possibly some dyestuffs, to form vile, persistent odors.

Sulfuryl fluoride (SO_2F_2) (F.W. 102) is a compressed gas marketed in cylinders under the trade name Vikane [6] and is said to be an excellent termite control fumigant. Although its molecular activity is approximately the same as methyl bromide, it is not rated as good for destruction of the insect egg stage. This may be because of a probably lower poisoning effect and because it is less soluble than the bromides.

The gas is more easily contained in fumigating chambers and by plastic bags than ethylene oxide and does not leave unpleasant residues or damaging after-effects such as have been attributed to the bromides.

There are two widely used and readily available moth repellents. One, which has been used in quantity, is naphthalene, a cyclic hydrocarbon ($C_{10}H_8$), obtained from coal tar and is purchasable as the familiar moth balls of years past. As used, it is a solid material which sublimes or vaporizes at ordinary temperature without passing through the liquid phase. There are some doubts as to the actual toxic effects of the vapor on insects, especially in the egg stage, so that the principal value of this agent is that of discouraging the adult moths from approaching the treated fabrics. Perhaps its greatest value is psychological on the user, because the penetrating unpleasant odor produces a sense of accomplishment.

Paradichlorobenzene ($C_6H_4Cl_2$) is a more modern substitute for naphthalene and is used in a similar way. The solid crystals do not melt below 53°C (127° F.), but there is a definite vapor pressure which causes sublimation at ordinary temperatures. This will produce a gas concentration which is probably just high enough if confined in a closed space to kill the adult moths and larvae. Because furniture and carpet beetles are more hardy, there is some doubt as to its certain effect on them. The molecule is probably too heavy (F.W. 146) and too large because of its globular shape to penetrate insect membrane easily; and since the probable concentration in air under most circumstances would be quite low, we predict that it would not be effective on the eggs. Although it is quite toxic to human beings in high concentration, we do not expect harmful effects from the air mixture usually encountered. Although its odor is more bearable to human beings than naphthalene, it may be repellent to moth life and for that reason has a limited protective value.

NOTES

[1] "Carboxide" 90% carbon dioxide and 10% ethylene oxide is marketed by Union Carbide and Carbon Chemicals Co. A similar product known as a sterilizing mixture is put out by the Mathieson Company, Inc.

[2] "Cryoxcide" is a registered trade mark of the American Sterilizer Co. of Erie, Pa. for 11% ethylene oxide, 44.5% dichlorodifluoromenthane and 44.5% trichloromonofluoromethane (one of a series of "Freons"—trade named products of the E. I. du Pont de Nemours Company). Other sterilizing gases resembling "Cryoxcide" are "Steroxcide", a product of the Wilmot Castle Co., Rochester, N. Y., and "Benvicide" licensed by Bienvenue Laboratories and sold by Mathieson Co., Inc.

[3] Leopold Shieflan and Morris B. Jacobs, *Handbook of Solvents*, D. Van Nostrand Co., Inc., 1953 (as revised).

[4] *Dow Technical Manual*, Dow Chemical Co., Midland, Michigan.

[5] *Encyclopedia of Chemical Technology*. Editors: Raymond E. Kirk and Donald F. Othmer. Published by Inter-Science Encyclopedia, Inc. (First edition copyrighted in 1947.)

[6] Henry E. Gray, *Fumigating with Vikane*, Dow Chemical Co., Midland, Michigan. Paper presented to 12th International Congress of Entomology, London, England, 1964.